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PROTECTIVE COATING FOR AUTOMOTIVE TRIM PIECES AND METHOD OF MAKING THE SAME

Microfiche Appendix

[0001] Not Applicable.

Field of the Invention

[0002] The present invention generally relates to the field of protective coatings and in particular to protective coatings for aluminum or aluminum alloy surfaces.

Background of the Invention

[0003] Anodically produced oxide layers are frequently applied to aluminum surfaces to protect the aluminum or aluminum alloys against weathering and/or corrosion. A number of processes, such as anodizing, are known for the application of anodic oxide layers to aluminum. These oxide layers protect the aluminum surface from the effects of weather and other corroding media. In addition, anodic oxide layers also provide a harder surface thereby giving the aluminum an increased resistance to wear.

[0004] Anodizing is an electrochemical conversion process wherein a coating of aluminum oxide is grown from aluminum on a surface of an aluminum article. The anodizing of aluminum is performed by making the aluminum article the anode or positive end of an electrical circuit within an acid electrolyte in which the aluminum article is immersed. By passing an electrical current through the acid electrolyte from the cathode, an aluminum oxide layer develops on the surface of the aluminum article. This aluminum oxide layer can be formed so that it has a porous quality. The aluminum oxide layer can be dyed in a variety of colors. The coating thickness and surface characteristics are controlled to meet the desired specifications of the final product.

[0005] Another method of providing protection from weathering is by electrodeposition coating. Electrodeposition coating is widely used for primer coating of cars, household electric appliances, and industrial machines. Electrodeposition coating has a good efficiency in application and a high corrosion resistance and can also minimize risk of environmental contamination because water is employed as a solvent.

[0006] Cationic electrodeposition provides excellent corrosion-protective coatings for automobiles and for appliances while diminishing the usage of volatile organic solvents required for painting. It has been used as an undercoating method of articles to be coated which are large and complicated in shape and are required to have high rust prevention, such as car bodies. Cationic electrodeposition is capable of coating intricately shaped articles in an automated and continuous manner. As compared with other coating methods, the technology is highly efficient in coating consumption, hence economical, and has come into wide use as an industrial coating method.

[0007] Cationic electrodeposition of water-soluble compositions utilizes a direct current to cause positively charged electrolytes in an aqueous medium to form a coating on the cathode. The electrolytes are usually polymers, e.g. acrylic and/or epoxy polymers. The positively charged polymers are dispersed in an aqueous medium such that upon applying a voltage between an article having a conductive surface serving as a cathode and a counter-electrode both of which are in contact with the aqueous medium, the positively charged polymer migrates to the conductive surface. There the polymer loses its charge, becomes insoluble and forms an insulating film on the conductive surface. As the deposition progresses, the conductive surface becomes insulated which advantageously allows uniform coating over even remote areas, i.e. interior or recessed areas.

[0008] Furthermore, cathodic electrodeposition provides excellent coatings for corrosion protection of automobiles and appliances while diminishing the usage of volatile organic solvents required for painting. Where metals are electrocoated, pretreatment is required to obtain optimal corrosion resistance for the coating. A

chrome rinse is usually used as a pretreatment. However, chromium or chromium compounds have a high toxicity and hence it is desirable to provide an electrocoating method that does not require a chrome pretreatment.

[0009] The present invention is directed to improving the appearance of anodized aluminum and protecting it from corrosion, stains and weathering. It had previously been proposed to protect anodized aluminum by means of a clear coating, but the performance of prior art coatings has not been as good as desired, particularly with regard to adhesion. It is believed that anodizing tends to seal the surface irregularities of an aluminum surface, thereby making it more difficult for a subsequently applied coating to adhere. As a result, prior art clear coatings on anodized aluminum have typically failed in relatively short periods of time by chipping and peeling, which not only leaves the anodized layer exposed to corrosion, but also produces an unattractive appearance.

[0010] Coatings based on a variety of film-forming resin systems are generally considered appropriate for coating aluminum surfaces, including alkyds, polyesters, silicone-polyesters, thermoplastic acrylics, thermosetting acrylics, and fluoropolymers. When used on anodized aluminum surfaces, however, most of these conventional coating compositions do not exhibit the desired degree of adhesion to the anodized surface. A variety of additives for promoting adhesion to an anodized aluminum surface are available commercially.

[0011] There are two types of electrocoating compositions that are based on epoxy resins and acrylic resins. However, it has been found that epoxy-based electrocoats start to peel and discolor after a relatively small period of time, e.g. about six months. Furthermore, epoxy resins are not UV stable and hence they are not suited for exterior applications, such as on automotive trim pieces and in particular on class "A" surfaces.

[0012] Another problem with the application of an electrocoat over top of anodized aluminum occurs during the thermal curing step of the electrocoat. The high curing

temperatures crack or craze anodic oxide coatings on aluminum because the thermal expansion of these oxide coatings is significantly lower than that of the underlying aluminum base metal. Craze lines extending through the anodic oxide film substantially detract from the protective and esthetic value of the anodic coating.

[0013] U.S. Patent No. 3,798,143 to Rolles et al. provides a method for an electrophoretic deposition of acrylic copolymers or interpolymers from aqueous colloidal dispersions on aluminum or anodized aluminum. This overcoat is applied directly on the anodized aluminum surface to seal the pores and to avoid additional step(s) of sealing the porous surface by means of a nickel seal or boiling in hot water. Furthermore, Rolles et al. eliminate the thermal curing step to avoid cracks or crazing of the anodic oxide film. This is done by employing an aqueous colloidal dispersion comprising an interpolymer of methyl methacrylate and an acid selected from the group of acrylic acid, methacrylic acid, maleic acid, and itaconic acid, and thereafter coalescing the resulting coating on the anodized aluminum. The coalescing is achieved by heating the coating at relatively low temperatures not exceeding 200°F. If a coalescing agent is employed, such as xylol or butyl Cellosolve, the coalescing may be accomplished at room temperature, or about 65-90°F. Thus, Rolles et al. employ temperatures to coalesce the resin films that are below those at which extensive crazing of anodic coatings occurs. However, the employed coalescing agents are carcinogens and hence not environmentally friendly.

[0014] Furthermore, it is desirable to provide a coating with improved corrosion resistance and weathering resistance/UV stability. In accordance with the present invention a thermosetting resin is electrodeposited over an anodized aluminum or aluminum alloy surface which requires relatively high temperatures for the thermal curing step of the electrocoat.

[0015] Hence it is further desirable to provide a method of coating over anodized aluminum or aluminum alloys that will maintain a substantially continuous underlying anodized layer, without cracks or crazing, during thermal curing of the thermosetting resin.

[0016] It is desirable to provide an electrolytic coating to an anodized aluminum surface.

Summary of the Invention

[0017] In accordance with one aspect of the invention there is provided, a method of providing a protective coating on a surface of an aluminum article comprising the steps of providing an anodized coating on the surface of the aluminum article, sealing pores of the anodized coating, electrocoating the anodized coating of the aluminum article with a thermosetting cationic acrylic resin, and curing the thermosetting cationic acrylic resin, wherein the anodized coating has a sufficient softness such that a curing of the thermosetting cationic acrylic resin does not cause a formation of fractures in the anodized coating.

[0018] In accordance with another aspect of the invention, the anodized coating is provided at a temperature between substantially about 20 to 30°C, at a voltage of substantially about 10 to 15V, and at an electrolyte concentration of substantially about 10 to 15% by volume. If desired, the electrolyte is sulfuric acid.

[0019] In accordance with a further aspect of the invention, the thermosetting cationic acrylic resin is a clear resin.

[0020] In accordance with another aspect of the invention, the thermosetting cationic acrylic resin comprises polyurethane.

[0021] In accordance with yet another aspect of the invention, the thermosetting cationic acrylic resin comprises a UV stabilizer. The step of curing is performed at a temperature of substantially about 163-177°C for substantially about 20 to 50 minutes.

[0022] In another aspect of the invention, the method further comprises the step of coloring the aluminum article after providing the anodized coating and prior to sealing pores of the anodized coating. The coloring step is an electrolytic coloring step using a metal salt as a colorant, such as cobalt sulfate and tin sulfate.

[0023] In accordance with the invention, there is further provided, a method of providing a protective coating for automotive trim pieces comprising the following steps anodizing the aluminum article at a temperature between substantially about 20 to 30°C, at a voltage of substantially about 10 to 15V, and at an electrolyte concentration of substantially about 10 to 15% by volume for providing a layer of aluminum oxide, said layer of aluminum oxide is a porous layer, sealing the porous layer of aluminum oxide for providing a sealed layer of aluminum oxide, electrocoating the sealed layer of aluminum oxide with a thermosetting cationic acrylic resin for providing an electrocoat, and curing the thermosetting cationic acrylic resin.

[0024] In accordance with another aspect of the invention, there is provided, an automotive trim piece having a protective coating, said protective coating comprising an aluminum or aluminum alloy base metal, a layer of aluminum oxide provided over top said aluminum or aluminum alloy base metal, and an electrocoat layer provided over top of said layer of aluminum oxide, said electrocoat layer comprising a clear thermosetting cationic acrylic resin, said layer of aluminum oxide having a softness so as to avoid fractures in said layer of aluminum oxide when the electrocoat layer is provided over top the layer of aluminum oxide.

[0025] In accordance with another embodiment of the invention, the automotive trim piece further comprises an electrolytic colorant in the layer of aluminum oxide.

[0026] Advantageously, the present invention provides a protective coating for a variety of aluminum articles, and in particular protection from weathering/UV light and corrosion. The protective coating in accordance with the invention is advantageously applied on exterior automotive trim pieces. The protective coating of the present invention has a good adhesion and does not fracture upon a thermal curing of an electrocoat layer that is applied over top of an anodized layer.

[0027] The electrodeposition step of the present invention provides a method that requires a lower usage of volatile organic solvents and hence it is more

environmentally friendly. In addition, the method of providing a protective coating on automotive trim pieces obviates a chrome pretreatment step.

Brief Description of the Drawings

[0028] Exemplary embodiments of the invention will now be described in conjunction with the following drawings wherein like numerals represent like elements, and wherein:

[0029] Fig. 1 presents a schematic drawing of an aluminum article having a protective coating in accordance with the present invention;

[0030] Fig. 2 shows a flow chart of the various cleaning and pretreating steps;

[0031] Fig. 3 shows a flow chart of the steps for a clear anodizing process;

[0032] Fig. 4 shows a flow chart of the steps for a color anodizing process;

[0033] Fig. 5 shows a flow chart of the electrocoating steps; and

[0034] Fig. 6 shows a flow chart of the steps for an alternative clear anodizing process wherein the anodized aluminum article is faintly colored.

Detailed Description of the Preferred Embodiments

[0035] The present invention provides a protective coating for an aluminum article and a method of making the same. The term aluminum as used herein is intended to include both aluminum and aluminum alloys. Advantageously, the protective coating in accordance with the present invention imparts corrosion and weathering protection to the coated aluminum article including ultra-violet (UV) stability. Initially, an aluminum article 12 is anodized to provide a layer of aluminum oxide 14 and subsequently it is provided with an electrocoat 16 by means of electrodeposition as

shown in Fig. 1. The method of providing the protective coating is explained hereinafter in further detail in conjunction with Figs. 2 to 6.

[0036] The anodizing step is typically performed by subjecting the aluminum article to anodic oxidation by passing a DC electric current through an acidic electrolyte solution, for example containing sulfuric acid (H_2SO_4), and between the aluminum article arranged as the anode and a cathode arranged as the counter-electrode, advantageously after degreasing. The electrolytic oxidation of the aluminum surface produces a protective oxide coating. The anodic coating consists of hydrated aluminum oxide which imparts resistance to corrosion and abrasion. The aluminum oxide coating is generally transparent but it may be colored.

[0037] Because anodic coatings are normally transparent, any modifications or improvements of the surface of the aluminum article to be anodized carry through the anodizing process. As a result, many process lines for anodizing alumina articles include pretreatment steps.

[0038] The pretreatment operations and the anodizing step are performed in a series of tanks and the aluminum article is moved from tank to tank. The aluminum article is rinsed thoroughly after each operation so as to avoid contamination and interference during the next processing step.

[0039] A typical process line for the anodizing step in accordance with the present invention includes cleaning steps, pretreating steps, an anodizing step, a coloring step (if desired), and sealing steps.

[0040] Turning now to Fig. 2, a flow chart is presented showing the various cleaning and pretreating steps. The aluminum article is loaded 100 on a rack and then passed to a first tank where an alkali cleaning step 102 is performed. The aluminum article is then rinsed 104 and subsequently an acid cleaning step 106 and a rinsing step 108 are performed. These cleaners remove, for example, fabrication oils, fats, greases and buffing compounds.

[0041] Following the cleaning steps, a pretreatment step is performed to improve the surface of the aluminum article prior to the anodizing step. In accordance with the present invention a bright dip step 110 is used as a pretreatment step. The bright dip process takes place in a bath of mixed acids to impart a bright, shiny finish by chemically polishing the surface of the aluminum article so as to level microscopic peaks and valleys on the surface. The bright dip step is usually preceded by an acid cleaning, as indicated by reference numeral 106, to remove an oxide layer from the surface of the aluminum article so as to provide a uniform surface finish. Bright dip anodizing enhances the glossy appearance of aluminum for exterior ornamentation applications on class A surfaces. It achieves a highly electro polish finish similar to the quality of plating. In contrast to plating, bright dip is a chemical process that brightens aluminum and does not leave deposits on the surface of the part. After the aluminum article is bright dipped, it can be anodized clear or dyed to a variety of colors.

[0042] Following the bright dip 110, the aluminum article undergoes a drag out rinse 112 as a quick bright dip rinse followed by a clean rinse 114. After the bright dip 110 and rinsing steps 112 and 114, the aluminum article is dipped into a deoxidizer solution 116 to remove any residues of alloying agents or oxides. Following the deoxidizing step 116, the aluminum article is first rinsed 118 and then spray rinsed 120. Subsequently, the anodizing step is performed.

[0043] The anodizing step is the step that produces the actual alumina coating. It is performed in an electrolytic cell using sulfuric acid as the electrolyte. The aluminum article is made the anode (positive electrode). When a direct current (DC) is passed through the electrolytic cell, water is decomposed to form oxygen on the surface of the aluminum article. The oxygen reacts with the aluminum to form a porous layer of aluminum oxide. The thickness of this aluminum oxide coating is determined by the electrical current and the length of time it is applied.

[0044] In accordance with the present invention, a clear or color anodizing step is performed, depending on whether the anodized aluminum article is to be colored or to

remain clear. If a coloring of the anodized aluminum article is to be performed, the anodizing step is performed for a longer period of time so as to grow a thicker film that is suitable for coloring. In accordance with the invention, the anodizing step is typically performed between about 8 to 24 minutes.

[0045] In accordance with a further embodiment of the invention, the alumina film produced on the surface of the aluminum article needs to have a certain degree of softness so that this anodic oxide coating on the aluminum article maintains continuity and does not crack or craze when the subsequently applied electrocoat is cured at elevated temperatures. The softness of the alumina film is affected by the temperature of the anodizing bath, the voltage used during the anodizing step and the concentration of the electrolyte. During conventional sulfuric acid anodizing, the article to be anodized is immersed in a solution at a temperature of about 18-20°C with an electrolyte concentration of about 15-18% by weight and anodized at a voltage of about 18 V DC. In accordance with the present invention, it was found that the alumina film formed during the anodizing step has a sufficient softness when the anodizing step is performed between about 20-30°C at a voltage of 10-15V with an electrolyte concentration of 10-15% by volume. In other words, the anodizing step is performed at a higher temperature and a lower voltage in comparison to conventional anodizing. This produces an anodic oxide film having a greater density with more cell pores per area. Generally, the use of low acid concentrations and temperature favor a less porous, harder coating with the opposite favoring a more porous, softer coating. Sulfuric acid anodizing provides good corrosion protection and resistance to wear. In addition, it provides the possibility to color the anodized aluminum with a wide variety of colorants.

[0046] If desired, a commercial liquid additive to prevent burn marks at a contact point is added to the electrolyte bath at a concentration of 1-1.5% by volume. Such contact points occur for example where the racks contact the parts. This allows for an anodization at a higher temperature and improves a uniformity of the produced film thickness. The anodized part/electrolyte is much more forgiven for temperature stratification.

[0047] Hard coat anodizing on the other hand usually produces a very thick and hard anodic coating. This is accomplished with a bath similar to the sulfuric anodizing process but with the solution temperature reduced to about 0°C to slow the dissolution rate. A higher voltage of about 50 V DC is applied to enable the coating to continue to build after the insulation value of the coating starts slowing down the coating formation. The lower solution temperature and the higher voltage produce a dense crystal with small pore size. Such coatings, for example, would not have the degree of softness that is needed to ensure a continuity of the anodic oxide coating during a thermal curing of the subsequently applied electrocoat.

[0048] Soft anodizing is the most effective type of anodizing with respect to ornamental applications because it is available for the various color treatments together with corrosion protection. However, soft anodizing is often not a desirable type of anodizing due to the fact that it scratches easily when compared to conventional or hard anodizing.

[0049] Thus, in accordance with the invention the anodized layer should have a degree of softness/flexibility so as to maintain a continuity during a thermal curing of a subsequently applied electrocoat. This means that the anodic aluminum oxide coating does not fracture during the thermal curing step of an electrocoat applied over top of the anodic oxide coating.

[0050] Turning now to Fig. 3, a flow chart is presented showing the steps for a clear anodizing process. The aluminum article is anodized 200 and then rinsed three times with water 202, 204, 206. After the actual anodizing and rinsing steps are performed, the micro pores in the freshly anodized alumina coating are sealed or closed to provide a smooth, corrosion resistant surface. In accordance with the invention, a Nickel Pre-Seal 208 is performed first, followed by a nickel rinse 210. Then, a hot water seal 212 is performed, followed by rinsing steps 214, 216, and 218. The sealing steps convert the amorphous aluminum oxide to a more stable crystalline hydrate form to close off the pores in the anodized coating on the surface of the aluminum article and hence sealing it.

[0051] Fig. 4 shows a flow chart presenting the steps for a color anodizing process. Again, the aluminum article is first anodized 300 followed by rinsing steps 302, 304, and 306. However, the aluminum article undergoes a coloring process before the freshly anodized pores in the alumina coating are sealed. In accordance with the invention, an electrolytic coloring step 308 is performed by immersing the aluminum article after the anodizing step in a bath containing an inorganic metal salt. A current is applied to deposit the metal salt in the pores of the freshly anodized alumina coating. The resulting color depends on the metal used. Commonly used metal salts include cobalt sulfate, tin sulfate, nickel salts, and copper salts. The coloring step 308 takes advantage of the fact that the freshly anodized alumina coating is porous and hence capable of absorbing the colorants. In accordance with the invention, the deposited metal salt is conductive. This ensures a conductivity of the anodized coating which facilitates the further application of an electrocoat. The colored aluminum article is then rinsed in steps 310 and 312. Subsequently, the pores of the freshly anodized and colored alumina coating are sealed, as explained heretofore in conjunction with Fig. 3, by a nickel pre-seal 314, followed by a nickel rinse 316, followed by a hot water seal 318, followed by rinsing steps 320, 322, and 324. The sealing steps also seal the colorant in the coating thus preventing a loss of the colorant and/or an absorption of unwanted stains later on. Further, as explained heretofore, a sealed coating also has a higher corrosion resistance.

[0052] Having regard to Fig. 5, a flow chart representing the electrocoating steps is presented. At first, the previously anodized aluminum article undergoes an electrocoating step 400 wherein paint particles are deposited on the anodized aluminum article to form an even and continuous film over the surface of the anodized aluminum article. In accordance with the present invention a water-soluble thermosetting clear cationic acrylic electrocoating composition is used containing about 80-90% deionized water and about 10-20% paint solids. By the term "clear" is meant that the electrocoating is free of noticeable haze and yellowing following thermal treatment. Furthermore, the electrocoating material includes a UV-stabilizer to provide protection from weathering. The function of the UV light stabilizer is to protect the long-term degradation from all forms of wavelength of light. Today,

stabilizer packages utilizing a combination of UV absorbers and hindered amine light stabilizers (HALS) are state of the art for the protection of coatings. UV absorbers (UVA) filter out harmful UV light and HALS act as radical scavengers. The four most important UVA classes are hydroxy-benzophenones, oxanilides, hydroxyphenyl-benzotriazoles (BTZ) and hydroxyphenyl-s-triazines (HPT). HALS are based on a tetra-methyl-piperidine structure. After the electrodeposition of the electrocoat on the anodized aluminum article is finished, two ultrafiltrate rinsing steps 402 and 404 are performed to remove excess paint solids and provide a smoother finish appearance. The use of ultrafilters produces a permeate for rinsing and allows for a recovery of the excess paint solids. The rinsing steps are followed by a curing step 406 in an oven to cross-link and cure the electrocoat film over the anodized aluminum article. In doing so, the electrocoat film is baked at 325-350°F (163-177°C) for 20 to 50 minutes. Then, the electrocoated anodized aluminum article is allowed to cool and transferred 408 to a customer or assembly line.

[0053] In accordance with yet a further embodiment of the invention, the aluminum article is faintly colored using a blue or black dye. Fig. 6 shows a flow chart of the steps for such an alternative clear anodizing process wherein the anodized aluminum article is faintly colored. After an anodizing step 600 and rinsing steps 602, the freshly anodized aluminum article is immersed in a solution containing the dissolved dye to perform a dye coloring step 604. The porous alumina coating absorbs the dye. The intensity of the color is dependent on the dye concentration, immersion time, and temperature. In accordance with this embodiment of the invention, the dye concentration is relatively small yielding a blue undertone so as to create a chrome-like appearance of the anodized aluminum article. Following the dye coloring step 604, the aluminum article is rinsed 606 and the pores are sealed by means of a nickel pre-seal 608 and nickel rinse 610 followed by a hot water seal 612 and rinsing steps 614 as described heretofore.

[0054] The following examples are provided to further illustrate the process of the present invention, but these are not to be regarded as limiting.

Example I

[0055] An aluminum article was subjected to pretreatment steps in which it was degreased and cleaned by dipping it for 12 minutes in a commercially available alkali cleaner (pH=9) heated to 50±5°C; rinsed with water for 6 minutes at ambient; cleaned by dipping it for 3 minutes into a commercially available acid cleaner (based on phosphoric acid) heated to 45±5°C; rinsed with water for 3 minutes at ambient; bright dipped by immersing the aluminum article for 3.5 minutes in a commercially available bright dip solution (based on phosphoric acid) heated to 99±3°C to polish the aluminum article; drag out rinsed for 3 minutes with water heated to 30±5°C; rinsed with water for 3 minutes at ambient; deoxidized by dipping the article for 3 minutes into a commercially available deoxidizer solution (acid) at ambient to remove leftovers from the bright dip step; rinsed with water for 3 minutes at ambient; and spray rinsed with water for 3 minutes at ambient. If desired, the water used in the various rinsing steps is distilled or deionized water. The pretreated aluminum article was then subjected to clear anodization using a 12-13 volume % sulfuric acid electrolyte operated with a DC 13V source at a current density of 15-17 amps/ft.^{2} at a bath temperature of 23°C. However, the current density is dependent on the surface are of the aluminum article to be coated and as the surface area increases so does the current density (amperage). The aluminum article was thus anodized for 9 minutes. The anodized layer has a thickness of about 0.3-0.4 mils or 7.5-10 microns.

[0056] The described conditions provide a freshly anodized alumina coating on the surface of the article that has a sufficient degree of softness so that the thermal curing of a subsequently applied electrocoat over top of the alumina coating does not craze or fracture the alumina coating, maintaining a continuous layer. Thereafter, the aluminum article was rinsed three times with water for 6 minutes at ambient. The aluminum article was then subjected to a nickel pre-seal for a period of 3 minutes using a nickel acetate solution and then rinsed with deionized water. The nickel pre-seal acts as a catalyst for the subsequently applied hot water seal by subjecting the aluminum article for 6 minutes to boiling deionized water. Thereafter, the aluminum

article was washed three times for a period of 6 minutes by means of reverse osmosis rinse.

[0057] The aluminum article was then placed in an electrocoat tank containing a thermosetting clear cationic acrylic electrocoat composition and subjected to electrodeposition for 3 minutes at 50-125 V at a temperature of 26±2°C and a pH of 5.0±0.2. The conductivity was 500-650 microSiemens for a total dissolved solids contents of 10-15%. The employed electrocoating material is Powercron™ 935C, an electrocoating composition commercially available from PPG Industries, Inc. Typically, the electrocoating composition includes approximately 80-90% deionized water, 0-5% solvents, 1-10% pigments, 10-15% resins. The electrocoating composition contains an acrylic polyurethane modified with an ultraviolet (UV) stabilizer to provide UV/weathering resistance in addition to corrosion resistance.

[0058] After electrocoating, the aluminum article was subjected to two ultrafiltrate rinse cycles for a period of 3 minutes per cycle. Ultrafiltration produces a permeate for rinsing and allows for a recycling of the excess resin. The aluminum article was then baked in an oven for 48 minutes at 350 F (177°C) to crosslink and cure the acrylic electrocoat. Usually, 20 to 50 minutes are required for the thermal curing of the electrocoat with a minimum of 20 minutes. Thereafter, the anodized and electrocoated aluminum article is allowed to cool and can be transferred to a customer. The anodized layer maintains a continuous surface without cracks being formed or crazing occurring even after the electrocoat is baked at the curing temperatures of the thermosetting resin.

[0059] The present invention provides excellent coatings on the protected aluminum surfaces having good adhesion and wear resistance as well as strong UV light and corrosion resistance against alkali solutions, acid solutions, saline solutions, and the like.

Example II

[0060] The aluminum article was cleaned and pretreated as described in example I. The pretreated aluminum article was then subjected to color anodization using a 12-13 volume % sulfuric acid electrolyte operated with a DC 13V source at a current density of 15-17 amps/ft.^{2} at a bath temperature of 23°C. However, in accordance with an embodiment of the invention, the aluminum article was color anodized, i.e. the aluminum article was anodized for a longer period of time as described in example I, viz. for a period of 12 minutes. The longer anodization time provides a thicker alumina coating with deeper pores on the surface of the aluminum article for the following coloring step. Thereafter, the alumina article was washed by rinsing it three times with water for 6 minutes at ambient followed by electrolytic coloring using cobalt sulfate at a concentration of 110-120 g/l. The cobalt coloring was performed for 20±2 minutes at a voltage of 16±2 V AC and at a temperature of 22±2°C. During the cobalt coloring step, cobalt is electrolytically deposited into the pores of the freshly anodized coating yielding a black appearance of the aluminum article. The thus anodized and black colored aluminum article was washed twice by rinsing with water for 6 minutes at ambient. Thereafter, the pores of the freshly anodized coating on the aluminum article were sealed (nickel pre-seal and a hot water seal) and electrocoated as described in example I.

Example III

[0061] The aluminum article was anodized for 24 minutes during the clear and color anodization steps.

Example IV

[0062] The aluminum article was treated as described in example I. Prior to the electrocoating step, however, the anodized aluminum article was colored for 2-3 minutes at a bath temperature of about 40°C using a small amount of a black metal complex of an azo dye, and then rinsed four times with deionized water for about 6 minutes followed by the sealing steps as described in example I. The concentration of the dye was 0.068 g/l ± 0.002 g/l. Using such a small amount of colorant yields an

anodized aluminum article of clear appearance having a blue undertone with a generally clear silvery look, thus creating a chrome-like appearance.

[0063] The above described embodiments of the invention are intended to be examples of the present invention and numerous modifications, variations, and adaptations may be made to the particular embodiments of the invention without departing from the scope of the invention, which is defined in the claims.